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DESORPTION KINETICS OF FLUORANTHENE AND TRIFLURALIN FROM LAKE HURON AND LAKE ERIE, USA, SEDIMENTS

MARC S. GREENBERG,*†‡ G. ALLEN BURTON, JR.,† PETER F. LANDRUM,§ MATTI T. LEPPÄNEN,‖ and JUSSI V. K. KUKKONEN‖

†Institute for Environmental Quality, Wright State University, Dayton, Ohio 45435, USA
‡Biomedical Sciences, Wright State University, Dayton, Ohio 45435, USA
§Great Lakes Environmental Research Laboratory, National Oceanic and Atmospheric Administration, Ann Arbor, Michigan 48109, USA
‖Department of Biology, University of Joensuu, 80101, Joensuu, Finland

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Abstract—Desorption kinetics were determined for fluoranthene (FLU) and trifluralin (TF) spiked onto Lake Erie and Lake Huron, USA, sediments at three concentrations (10, 40, 100 mg/kg dry wt). Following four months of equilibration, desorption was measured by extraction with Tenax® and the data were fit to a first-order three-compartment kinetic model. The rate constants of the rapidly (k_{rap}), slowly (k_{slow}), and very slowly (k_{vs}) desorbing fractions were on the order of 10^{-1}/h, 10^{-2-3}/h, and 10^{-4}/h, respectively. The $t_{99.9}$ (time required for 99.9% of the FLU and TF to desorb from each pool value) for each compartment indicated that FLU and TF desorption from rapid, slow, and very slow compartments were on the order of hours, days, and years, respectively. Higher rates of desorption were observed for FLU and TF from the Lake Huron sediments and this was not apparently related to the total organic carbon (TOC), particle size distribution, or polarity (carbon-to-nitrogen ratio) of the sediments. In general, the total fraction of the initial contaminant amounts that desorbed over the time course was directly related to concentration, which we hypothesized was due to the combined effects of saturation of high-energy (slow and very slow) binding sites in the organic carbon matrix and hysteresis. In extrapolations to field conditions, FLU and TF were predicted to persist in the sediments for years due to the very slow desorption of an estimated 31 to 53% of the bulk concentrations. Based on the rapidly desorbing fractions, the bioavailable amounts of the contaminants were predicted to be between 31 to 55% of bulk sediment concentrations.

Keywords—Desorption kinetics Sediment Model Tenax® extraction Organic contaminants

INTRODUCTION

The sorption of organic contaminants by sediments is an important environmental fate process, as it can greatly influence the bioavailability and hence the effects and/or biodegradation of pollutants [1,2]. Ecological risk assessment of contaminated sediments is often based on whole sediment concentrations of hydrophobic organic chemicals, but several studies have shown that bioavailability, biodegradation, and toxic effects decrease with increasing contact time between contaminants and sediment particles [3,4]. This is thought to occur due to the process of sequestration, or the formation of contaminant fractions that are resistant to desorption [5]. Thus, using bulk sediment concentrations in environmental assessments may overestimate risk to aquatic species [4].

Although the importance of sediment aging and contaminant sequestration has been identified, the processes behind the formation of resistant desorption compartments are not well understood. Some proposed mechanisms include chemical nonequilibrium reactions between functional groups on the sorbent and sorbate, slow diffusion through intraparticle micropores, diffusion in the organic matter matrix, and entrapment [6,7]. Regardless of the exact mechanism, sequestration of contaminants has been shown to result in slowly desorbing fractions within the sediments that can persist for years [6]. Current kinetic models of contaminant desorption include triphasic models that describe rapidly, slowly, and very slowly desorbing fractions [8].

Desorption of contaminants from sediment particles is identified as a major process in the bioaccumulation of contaminants by benthic organisms [9–12]. In particular, it is desorption from a rapidly desorbed pool of contaminant that contributes to the bioaccumulation and dictates the bioavailability of the nonpolar organic contaminants. Recent method development allows for the measurement of the desorption kinetics from sediments using a Tenax® (Alltech, Deerfield, IL, USA) extraction technique [13]. This technique provides estimates of the rate coefficients and capacities of different binding pools within the sediment matrix particularly defining the fractions that may be readily bioavailable. When considering the importance of desorption from sediments in light of its utility in toxicity studies, the impact of differing sediment concentrations becomes an important focus. If there are a limited number of high energy (i.e., stronger sorbing) binding sites, then as the concentration of contaminant increases in sediments, a larger portion may be available to desorb and become bioavailable. This may be one of the mechanisms that complicates the use of sediment concentrations directly as measures of dose for risk assessment [12].

In this study, the desorption kinetics of sediment-associated fluoranthene (FLU) and trifluralin (TF) were measured over a 34-d period. A three-phase model was used to estimate the rapidly, slowly, and very slowly desorbing fractions and their respective first-order desorption rate constants at three different treatment concentrations from two Great Lakes sediments.

* To whom correspondence may be addressed (greenberg.marc@epa.gov). The current address of M. Greenberg is U.S. Environmental Protection Agency, Environmental Response Team, 2890 Woodbridge Avenue, Building 18, MS-101, Edison, NJ 08837.

METHODS

Chemicals

Radiolabeled [G-^{3}H]FLU was purchased from Chemsyn Science Laboratories (Lenexa, KS, USA) with a specific activity of 721 mCi/mmol. The [Ring-UL-^{14}C]TF was purchased from Sigma Chemical (St. Louis, MO, USA) with a specific activity of 16.8 mCi/mmol. The purity of the radiolabeled TF was determined to be >98% by the manufacturer (January, 2001) and was used without further purification. The radiolabeled FLU was determined to be >96% pure by thin-layer chromatography on silica gel plates using a solvent system of hexane:ethyl ether (9:1, v/v). Tenax-TA (60–80 mesh; 177–250 μm), a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide, was purchased from Alltech Associates. Before use, the Tenax beads were washed with deionized water, acetone, and hexane (three times each; 10 ml/g) and dried overnight at 75°C.

Sediments

Bottom surface sediments were collected from Lake Huron Station 54 (MI, USA; 45°31′0″N, 83°25′0″W) with a Ponar grab. Sediments from Lake Erie (OH, USA; 49°39′49″N, 82°49′46″W) were collected with a Birge-Ekman dredge. Collected sediments were placed in plastic bags contained within insulated coolers and transported to the laboratory for storage at 4°C until use. The sediments were wet sieved to remove large debris by pressing the bulk sediments through a 1.0-mm sieve and the ≤1.0-mm particles were retained for experimental use.

Sediment wet:dry weight ratio and percent water were determined for the sieved sediments (n = 5 per sediment) by weighing a wet sediment sample (12–20 g) into a preweighed foil pan and then drying at 60°C to constant weight.

Sediment total organic carbon (TOC) and total nitrogen contents as a percentage (±1 standard deviation; n = 3) of total dry sediment weight were determined by elemental analysis after acidification to remove carbonates on a Carlo Erba Instruments EA 1110 CHN analyzer (ThermoQuest Italia, Milan, Italy).

Particle-size distribution of the test sediments was determined by wet sieving in quadruplicate, 10-g samples of each sediment (n = 4) with filtered Lake Michigan water, drying the fractions to constant weight, and then calculating the mean percentage by mass (±1 standard deviation) for each size class. Sieve sizes used in particle separation were no. 40, 425 μm; no. 140, 106 μm; no. 230, 63 μm; no. 400, 38 μm; and no. 635, 20 μm.

Spiking

Solutions of radiolabeled and unlabeled FLU and TF were spiked onto Lake Huron and Lake Erie sediments at nominal concentrations of 10, 40, and 100 mg/kg dry weight of each test compound. Stock spiking solutions (50 ml) of FLU and TF in acetone were prepared for each sediment concentration by combining [^{3}H]FLU and [^{14}C]TF and the appropriate amount of unlabeled compounds in acetone. Target activity levels of radioisotopes in the sediments were 15,000 disintegrations per minute per gram (dpm/g) wet sediment for ^{3}H and 7,500 dpm/g wet sediment of ^{14}C. Duplicate 25-μl samples of each stock solution were placed into 12 ml of scintillation cocktail (Ultima Gold®; Packard BioScience, Groningen, The Netherlands) and analyzed by liquid scintillation counting (see *Analytical method* below). The mean values were used to calculate the new specific activities of the spiking solutions (μCi of radiolabeled compound/μmol of total nominal compound).

Sediments were spiked with FLU and TF using a modification of the rolling-jar method [14]. The stock solutions (50 ml) were added to 1-gal (3.785-L) glass jars containing 2 g of sand and rolled until the acetone carrier was evaporated, coating the sand and inside walls of the jars with FLU and TF. Sediments (0.77–2.22 kg wet wt) along with 1.5 ml of culture water per 25 g wet sediment were added to the jars and the mixture was rolled for 3 h at room temperature, held overnight at 4°C, and rolled the next day for 5 h. The sediments were then stored at 4°C for approximately four months to allow for dissolution and partitioning of the spiked compounds to occur [15]. Solution preparation and spiking were conducted at room temperature under constant yellow light ($\lambda > 500$ nm) to avoid potential photodegradation of FLU and TF.

Prior to the start of the experiment, spiked sediments were rolled again for 5 to 10 min to thoroughly mix the sediments with any water that had exuded during storage. Three replicate sediment samples were taken from each concentration for liquid scintillation counting, wet-to-dry-weight determination, and to determine the thoroughness of mixing. Wet sediment samples (100 mg) were placed into scintillation vials and 1.0 ml tissue solubilizer (Soluene®-350; Packard Bioscience) was added. The solubilizer was added to digest organic matter, thus facilitating the extraction of the [^{3}H]- and [^{14}C]-labeled compounds from the sediment matrix. The vials were capped, gently vortexed, and held for 24 h prior to the addition of scintillation cocktail (12 ml; Ultima Gold). After addition of the cocktail, the sediment samples were then held for 48 h to allow the subsidence of chemiluminescence prior to measurement of ^{3}H and ^{14}C activity.

The potential degradation of the test compounds during equilibration was estimated from a first-order decay model using measured degradation data from bioaccumulation experiments conducted after approximately 60 d of equilibration [16]. The purity of the test compounds in the sediments at the start of the desorption experiments was estimated to be >95% for FLU and 68 to 78% for TF, which is known to rapidly degrade [17].

Desorption experiment using Tenax beads

Both FLU and TF desorption kinetics were determined at 22°C using a Tenax solid-phase extraction method [13,18]. Spiked sediments (2.0 g), 38 ml of culture water, 1.9 mg $HgCl_2$, and 150 mg of Tenax beads were added to 40-ml amber, screw-cap vials with Teflon®-lined closures. Triplicate vials for each of the treatment concentrations (10, 40, and 100 mg FLU and TF/kg dry wt) per sediment (i.e., Lakes Huron and Erie sediments) were prepared. The $HgCl_2$ (50 mg/L) was added to the vials to prevent any further microbial breakdown of the contaminants during the time course of the desorption experiment [8,19]. The vials were attached to the axles of a rolling mill and were continuously inverted (60 rpm) such that the sediments and Tenax beads were well mixed. The Tenax was refreshed at 12 sample times (2, 5, 9, 13, 24, 48, 96, 168, 288, 456, 672, and 816 h) for each of the test vials. At each sample time, the vials were removed and the Tenax separated from the sediment suspension. Because the Tenax beads float, removal of the beads from the vial was accomplished by using a solvent-washed spatula that was fashioned from a coiled piece of 0.8-mm outer-diameter copper wire. The Tenax beads were transferred to a 20-ml borosilicate glass scintillation vial;

12 ml of scintillation cocktail was added; and the vial was capped, gently vortexed, and held for 48 h prior to measurement of ^{3}H and ^{14}C activity by liquid scintillation counting.

After termination of desorption (at 816 h), samples of the remaining sediment (~100 mg) and overlying water (5 ml) were taken from each vial and analyzed by liquid scintillation counting to determine the mass balance. Sediment samples were processed as described above. The water samples were placed directly into 12 ml of scintillation cocktail. The contents were vortexed for 10 s and the samples were stored for >48 h in the dark at room temperature.

Analytical methods

The activity of the FLU and TF in the sediment, Tenax, and water samples was measured by liquid scintillation counting on a Tri-Carb Liquid Scintillation Analyzer (Model 2300 TR; Packard Instrument, Meriden, CT, USA). The liquid scintillation analyzer was run in dual counting mode utilizing the inclusion method for the determination of ^{3}H and ^{14}C activities in the samples [20]. Luminescence correction and static control options were utilized for the analyses. Each sample was counted for 20 min, and the data were corrected for quench using the external standards ratio method after correcting for background. The total amounts of FLU and TF equivalents (parent compound and breakdown products on a molar basis) in each sample were calculated using the nominal specific activities of the spiking solutions.

Desorption modeling

Desorption of FLU and TF from the sediments was described by the following first-order three-compartment (triphasic) model [9]:

$$S_t/S_0 = F_{rap}e^{-k_{rap}t} + F_{slow}e^{-k_{slow}t} + F_{vs}e^{-k_{vs}t} \quad (1)$$

where S_t and S_0 are the sediment-sorbed amounts of contaminant at time t (h) and at the start of the experiment, respectively (μmol); F_{rap}, F_{slow}, and F_{vs} are the fractions of the contaminant present in the rapidly, slowly, and very slowly desorbing sediment compartments at time zero, respectively; and k_{rap}, k_{slow}, and k_{vs} are the rate constants of rapid, slow, and very slow desorption, respectively (1/h). While there are likely many binding sites of differing binding strengths, this model has been found to be useful to partition the binding into three pools of relatively greater binding capacity (e.g., lower desorption rates) [8,9,21]. The use of a model containing only two types of sites results in fits to the data that are inferior to a model with three pools and has coefficients of determination in the range of 0.94 to 0.999.

Three assumptions were made in order to apply this model. First, the amounts of FLU and TF in the aqueous phase were assumed to be negligible. The assumption was operationally met by the addition of Tenax to the system that was expected to strip the water of any desorbed chemicals [13,18]. Second, it was assumed that the chemicals spiked onto the sediments were in either the rapidly, slowly, or very slowly desorbing sediment compartments such that $F_{rap} + F_{slow} + F_{vs} = 1$ and further the desorption from each compartment was assumed to be independent of the other compartments. The values of F_{rap}, F_{slow}, F_{vs}, k_{rap}, k_{slow}, and k_{vs} were determined by least squares nonlinear regression of the desorption time course data (i.e., S_t/S_0 vs t) using SYSTAT for Windows, Version 9 (SYSTAT, Evanston, IL, USA).

The time required for 99.9% of a given fraction of FLU or TF to desorb from the sediments was calculated as follows:

$$F_s e^{-k_s t_1} = (1 - 0.999)F_e^{-k_s t_2} \quad (2)$$

where the subscript x denotes the compartment of interest (e.g., rapidly, slowly, very slowly desorbing); t_1 represents the time at which 99.9% of this initial fractional amount of contaminant has desorbed (h); and t_2 represents time zero (0 h).

Statistical analysis

The modeling of desorption using the three-phase model described by Equation 1 results in the simultaneous estimation of six parameters from the desorption-time profile. Therefore, entire curves of desorption data were compared with an F test by the method of Ratkowsky [22]. This analysis operates on the hypothesis that common estimates of model parameters obtained by fitting the pooled data set (i.e., all concentrations within a sediment type, both sediments within a treatment concentration) are sufficient to describe individual data sets and are therefore invariant. This hypothesis is tested statistically by a one-tailed F test with an alpha of 0.05 [22].

RESULTS

Sediment characteristics

The two sediments were varied in their characteristics. The wet:dry ratios were 4.23 ± 0.01 and 5.46 ± 0.12 for the sieved Lakes Erie and Huron sediments, respectively. Lake Huron sediment TOC (mean range, 3.64–3.66%) and total nitrogen (0.56–0.62%) were higher than sediments from Lake Erie (TOC, 2.00–2.08%; total nitrogen, 0.33–0.35%) by factors of approximately 1.8 and 1.7, respectively. The carbon-to-nitrogen (C/N) ratios were very similar between Lake Erie (5.87–6.31) and Lake Huron (5.67–6.61). Size-class distributions were (Lake Erie, Lake Huron): >430 μm, 0.37 ± 0.14%, 0.67 ± 0.16%; 420 to 106 μm, 1.63 ± 0.06%, 8.45 ± 0.89%; 106 to 63 μm, 4.62 ± 4.16%, 3.27 ± 0.40%; 63 to 37 μm, 1.50 ± 0.14%, 7.94 ± 2.26%; 37 to 20 μm, 1.40 ± 0.25%, 10.58 ± 6.44%; <20 μm, 90.6 ± 3.71%, 69.1 ± 9.13%.

Sediment and test vial samples

The mean measured concentrations of FLU were between 81 and 97% of their target nominal concentrations for the Lake Erie sediments and 86 to 95% for Lake Huron sediments (Table 1). Trifluralin mean concentrations in the sediments were 71 to 85% and 76 to 84% of their target nominal concentrations in the Lakes Erie and Huron sediments, respectively (Table 1). In general, the percent of the target concentration achieved decreased with increasing treatment concentration. Based on measured sediment concentrations, the amounts of FLU and TF added to each vial were calculated for mass balance determination (Table 1).

At the end of the desorption experiment, the mass balance was determined for each replicate. In the Lake Erie sediment, the mass balances were 76.6 ± 1.65% for FLU and 94.8 ± 2.70% for TF; while for the Lake Huron sediment, the mass balances were 78.3 ± 1.61 and 96.4 ± 1.91% for FLU and TF, respectively.

Fractions and rate constants of desorption

The desorption curves (plotted as S_t/S_0 versus time) were characterized by a rapid decrease in the amount of contaminant sorbed to the sediments early, from 0 to 50 h, followed by a transition period between 50 to 200 h, after which desorption

Table 1. Concentrations of fluoranthene and trifluralin in sediments used for the desorption experiment and amounts of each chemical in the desorption vials at time = 0 h; samples from each treatment were taken in triplicate

		Concentration in sediments (mg/kg dry wt)		Amount in desorption vials (μg)	
	Nominal sediment concentration	Fluoranthene	Trifluralin	Fluoranthene	Trifluralin
Location	(mg/kg dry wt)	Mean ± SD[a]	Mean ± SD	Mean ± SD	Mean ± SD
Lake Erie, USA	10	9.67 ± 0.32	8.54 ± 0.39	4.63 ± 0.05	4.08 ± 0.04
	40	35.7 ± 0.21	32.1 ± 0.6	17.4 ± 0.04	15.7 ± 0.04
	100	80.5 ± 2.07	70.6 ± 2.4	39.3 ± 0.28	34.5 ± 0.25
Lake Huron, USA	10	9.09 ± 0.15	8.13 ± 0.06	3.47 ± 0.02	3.11 ± 0.02
	40	37.8 ± 0.52	33.4 ± 0.19	13.9 ± 0.09	12.3 ± 0.08
	100	86.0 ± 1.57	76.2 ± 1.03	31.8 ± 0.60	28.2 ± 0.53

[a] Standard deviation.

appeared to be very slow (Figs. 1 and 2). The desorption of FLU and TF in the sediments generally exhibited a pattern of less total desorption at the lower concentrations.

The size of the fractions of FLU and TF in the rapidly, slowly, and very slowly desorbing compartments and their rate constants are shown in Tables 2 and 3. The fits of the pooled data were in very good agreement with the individual treatment data sets (residual sum-of-squares range, 0.001–0.006; r^2 range, 0.994–0.999). Desorption rate constants, as expected, followed the progression of $k_{rap} > k_{slow} > k_{vs}$ and were generally on the order of 10^{-1}, 10^{-2}, and 10^{-4} per hour, respectively. In general, the slowly desorbing fraction (F_{slow}) of contaminants was the smallest compartment at ≤16.5% of total FLU and ≤18.2% of total TF in the sediments. The values of F_{rap} ranged across the sediments from 31.3 to 47.4% and 39.7 to 54.9% for FLU and TF, respectively. The very slowly desorbing fractions (F_{vs}) were similar to rapidly desorbing compartment and ranged from 40.6 to 52.9% for FLU and 30.5 to 42.0% for TF.

Statistical comparisons between the treatments in Lake Erie sediments resulted in rejection of the null hypothesis that the values of F_{rap}, F_{slow}, F_{vs}, k_{rap}, k_{slow}, and k_{vs} would be the same across the concentrations ($F_{18,103} = 30.0$, $p < 0.00001$ for FLU; $F_{18,142} = 146$, $p < 0.00001$ for TF). Comparisons of the desorption curves for FLU and TF from the Lake Huron sediments again rejected the null hypothesis of common parameter values across the treatment concentrations ($F_{18,111} = 164$, $p < 0.00001$ for FLU; $F_{18,111} = 23.5$, $p < 0.00001$ for TF). Supplementary statistical testing showed that all three initial fractional amounts (F_{rap}, F_{slow}, and F_{vs}) of desorbing FLU and F_{rap} and F_{vs} of desorbing TF were not equivalent across the three treatment concentrations (Lake Erie, all $F_{3,88} > 2.7$, $p \leq 0.03$; Lake Huron, all $F_{3,36} > 2.7$, $p \leq 0.03$).

Pairwise comparisons of the curves were performed between sediments with respect to dose (i.e., 10 mg/kg Lake Huron versus 10 mg/kg Lake Erie). Each of these six comparisons (three for each FLU and TF) resulted in a detection of significant differences ($F_{obs} > F_{crit}$; $p < 0.05$ [16]) between desorption in the two sediments, with the desorption rate constants of FLU and TF being faster in the Lake Huron sediments (Tables 2 and 3) compared with the Lake Erie sediments. The fractions of FLU and TF desorbing from the rapid, slow, and very slow desorption compartments did not exhibit any general trends between sediments.

Desorption time

The times required for 99.9% ($t_{99.9}$) of the FLU and TF to desorb from each pool were calculated from the corresponding desorption rate coefficients (Table 4). The times were on the

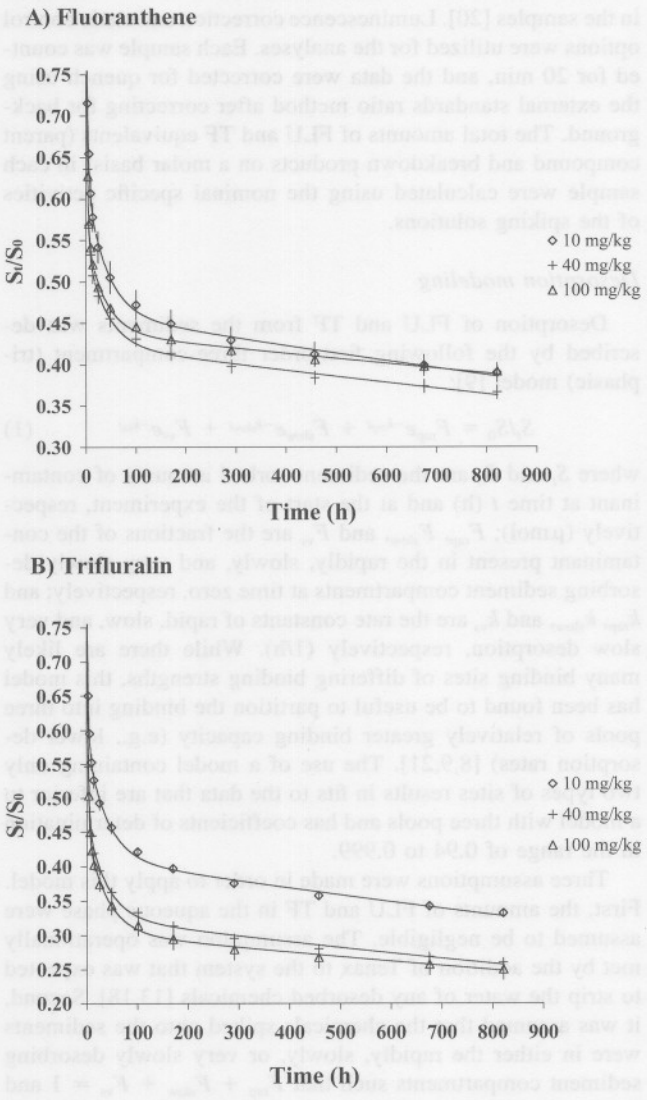

Fig. 1. Plots of the fractional mass (S_t/S_0) of (**A**) fluoranthene and (**B**) trifluralin in spiked Lake Erie, USA, sediments versus desorption time. Both S_t and S_0 are the sediment-sorbed amounts of contaminant at time t (h) and at the start of the experiment ($t = 0$), respectively. Measurements are indicated by symbols. Error bars represent the standard deviation of three samples. Solid lines represent best-fit model results.

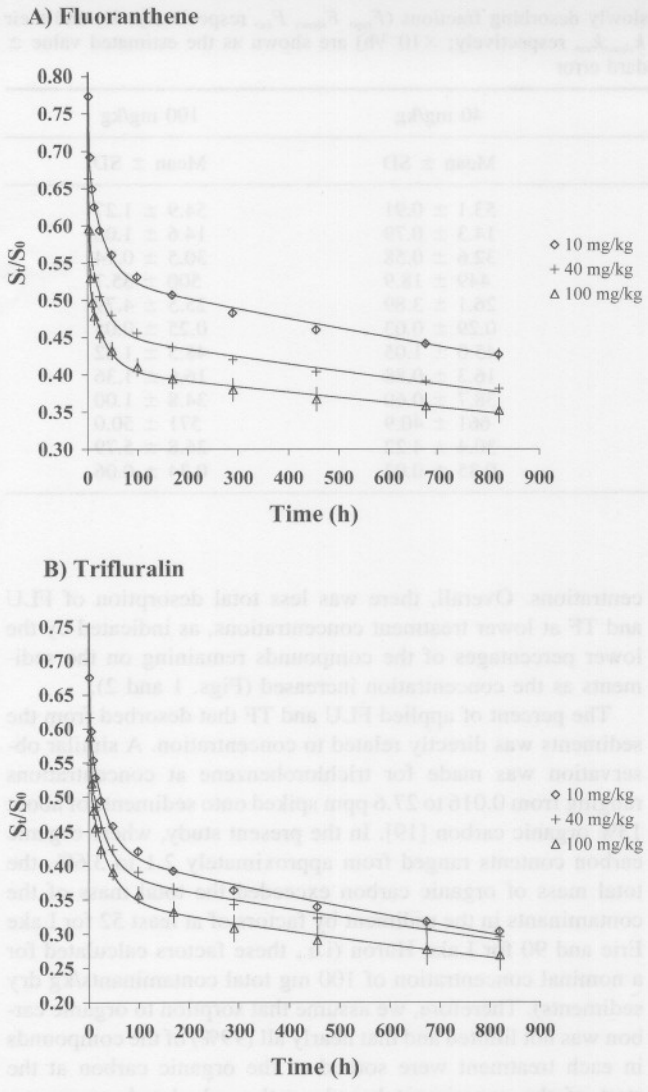

Fig. 2. Plots of the fractional mass (S_t/S_0) of (**A**) fluoranthene and (**B**) trifluralin in spiked Lake Huron, USA, sediments versus desorption time. Both S_t and S_0 are the sediment-sorbed amounts of contaminant at time t (h) and at the start of the experiment ($t = 0$), respectively. Measurements are indicated by symbols. Error bars represent the standard deviation of three samples. Solid lines represent best-fit model results.

order of hours, days, and years for contaminant desorption from the rapid, slow, and very slow compartments, respectively. As would be expected from the desorption rate constants, the shortest times are for the Lake Huron sediment compared with the Lake Erie sediments.

DISCUSSION

Triphasic desorption

The time frame for the desorption study was long enough to provide reasonable estimates of the rapid, slow, and very slow desorption of FLU and TF from Great Lakes sediments. The predicted $t_{99.9}$ values for rapid (≤20.3 h) and slow (≤11.5 d) desorption were less than the duration of the experiment, thus, these fractions and their corresponding desorption rates could be well characterized. In addition, 6 of the 12 samples were taken early, within the first 48 h of the time course, as recommended by Opdyke and Loehr [23], so that reliable estimates for F_{rap}, k_{rap}, F_{slow}, and k_{slow} would be obtained. However, there is some uncertainty in the estimates of k_{vs} values due to the relatively short duration of the experiment in relation to the time scale of very slow desorption, which is on the order of years [6,23]. The goodness-of-fit indicators of the model predictions to the data suggest that k_{vs} is at least as well characterized as k_{slow}. Even with this uncertainty, an increasing number of triphasic models have been described in the recent literature and found to be useful to describe the behavior of contaminants in sediments [8,9,19,21,24].

A more significant source of uncertainty that arises in these desorption measurements is due to the degradation of TF in the sediments during the four months prior to the initiation of the study (only 68–78% parent TF at $t = 0$ h). Therefore, the estimates of the fractions and rate constants of TF desorption from the sediments should be viewed with caution. Because many of the TF breakdown products are more polar and more easily extracted from soils than the parent compound [25], it is possible that the parameter estimates were misrepresented and that the values of F_{rap} and k_{rap} were overestimated. However, as discussed below, the parameters estimated in the present study compare favorably with previously reported desorption rate constants and fractions and thus should be useful estimates of desorption.

Table 2. Fluoranthene desorption parameters. The rapidly, slowly, and very slowly desorbing fractions (F_{rap}, F_{slow}, F_{vs}, respectively; %) and their corresponding rapid, slow, and very slow desorption rate constants (k_{rap}, k_{slow}, k_{vs}, respectively; × 10^{-3}/h) are shown as the estimated value ± asymptotic standard error

		10 mg/kg	40 mg/kg	100 mg/kg
Sediment	Parameter	Mean ± SD[a]	Mean ± SD	Mean ± SD
Lake Erie, USA	F_{rap}	37.2 ± 1.78	45.1 ± 1.03	43.8 ± 0.79
	F_{slow}	16.5 ± 1.52	12.4 ± 0.89	12.3 ± 0.66
	F_{vs}	46.2 ± 0.90	42.4 ± 0.60	43.9 ± 0.37
	k_{rap}	341 ± 32.1	387 ± 19.0	411 ± 17.7
	k_{slow}	25.0 ± 5.42	25.6 ± 4.81	27.5 ± 3.46
	k_{vs}	0.22 ± 0.04	0.19 ± 0.03	0.15 ± 0.02
Lake Huron, USA	F_{rap}	31.3 ± 0.92	41.4 ± 0.68	47.4 ± 1.46
	F_{slow}	15.6 ± 0.78	13.1 ± 0.57	11.9 ± 1.22
	F_{vs}	52.9 ± 0.47	45.4 ± 0.32	40.6 ± 0.73
	k_{rap}	520 ± 31.9	586 ± 22.3	591 ± 47.4
	k_{slow}	31.3 ± 3.82	34.2 ± 3.52	31.5 ± 7.88
	k_{vs}	0.27 ± 0.02	0.23 ± 0.01	0.19 ± 0.04

[a] Standard deviation.

Table 3. Trifluralin desorption parameters. The rapidly, slowly, and very slowly desorbing fractions (F_{rap}, F_{slow}, F_{vs}, respectively; %) and their corresponding rapid, slow, and very slow desorption rate constants (k_{rap}, k_{slow},k_{vs}, respectively; $\times 10^{-3}$/h) are shown as the estimated value ± asymptotic standard error

		10 mg/kg	40 mg/kg	100 mg/kg
Sediment	Parameter	Mean ± SD[a]	Mean ± SD	Mean ± SD
Lake Erie, USA	F_{rap}	41.7 ± 1.01	53.1 ± 0.91	54.9 ± 1.27
	F_{slow}	17.0 ± 0.85	14.3 ± 0.79	14.6 ± 1.06
	F_{vs}	41.2 ± 0.57	32.6 ± 0.58	30.5 ± 0.74
	k_{rap}	430 ± 24.4	449 ± 18.9	500 ± 35.7
	k_{slow}	25.6 ± 3.21	26.1 ± 3.89	25.5 ± 4.79
	k_{vs}	0.28 ± 0.03	0.29 ± 0.03	0.25 ± 0.05
Lake Huron, USA	F_{rap}	39.7 ± 0.99	45.0 ± 1.05	48.5 ± 1.62
	F_{slow}	18.2 ± 0.83	16.3 ± 0.88	16.6 ± 1.36
	F_{vs}	42.0 ± 0.58	38.7 ± 0.60	34.8 ± 1.00
	k_{rap}	701 ± 43.0	661 ± 40.9	571 ± 50.0
	k_{slow}	31.8 ± 3.75	30.4 ± 4.22	26.8 ± 5.79
	k_{vs}	0.42 ± 0.03	0.35 ± 0.03	0.34 ± 0.06

[a] Standard deviation.

Desorption rate constants

The rate constants of FLU and TF that were estimated to be desorbing rapidly, slowly, and very slowly were in reasonable accordance with values reported in other studies for polycyclic aromatic hydrocarbons spiked onto sediments. For sediments collected from Lake Oostvaardersplassen, The Netherlands, spiked with polycyclic aromatic hydrocarbons and allowed to equilibrate for 34 d, Cornelissen et al. [13] reported a k_{rap} of 0.202/h and a k_{slow} of 3.12×10^{-3}/h for FLU. The k_{rap} in that study was within a factor of two to three of the values obtained in the present study. However, the value of k_{slow} was an order of magnitude slower than the values estimated for the Great Lakes sediments [13]. In another study with the sediments from the same site, Cornelissen et al. [21] reported k_{slow} values of 3.12×10^{-3}/h and 128×10^{-3}/h at 20 and 65°C, respectively, and a k_{vs} of 4.1×10^{-3}/h at 65°C. Temperature elevation to 65°C [21] increased the rate constants of slow and very slow desorption to levels that were faster than those observed for FLU in the present study at 22°C by factors of about four to seven for k_{slow} and by an order of magnitude for k_{vs}.

The TF desorption from sediments and soils has not previously been investigated with the same continuous desorption methods as used in the present study and those cited above for FLU. However, Smith et al. [26] reported that 35 to 47% of the initial amount of TF had desorbed by a first-order process over 84 d, and there was no apparent effect of contact time because freshly spiked soils and those aged for 10 months following application of TF had similar rates. The average desorption half-life of TF from the soils was 103 d [26]. Total TF desorption was determined for Great Lakes sediment to be between 26 and 33% of the initial amounts in the sediments by 34 d, which is close to the amount predicted to desorb by day 34 based on Smith et al. [26].

Concentration dependence of the amount of contaminant desorbed

Statistical analysis of the curves (Figs. 1 and 2) for the sediment desorption data indicated that the values of the fractions of the desorbing compartments (Tables 2 and 3) were different between treatment concentrations of FLU and TF for a given sediment, but that the rate constants were the same. In general, we observed that F_{rap} increased with levels of FLU and TF, whereas both F_{slow} and F_{vs} decreased with the concentrations. Overall, there was less total desorption of FLU and TF at lower treatment concentrations, as indicated by the lower percentages of the compounds remaining on the sediments as the concentration increased (Figs. 1 and 2).

The percent of applied FLU and TF that desorbed from the sediments was directly related to concentration. A similar observation was made for trichlorobenzene at concentrations ranging from 0.016 to 27.6 ppm spiked onto sediments of about 13% organic carbon [19]. In the present study, where organic carbon contents ranged from approximately 2.1 to 3.6%, the total mass of organic carbon exceeded the total mass of the contaminants in the sediment by factors of at least 52 for Lake Erie and 90 for Lake Huron (i.e., these factors calculated for a nominal concentration of 100 mg total contaminants/kg dry sediments). Therefore, we assume that sorption to organic carbon was not limited and that nearly all (99%) of the compounds in each treatment were sorbed to the organic carbon at the start of the experiment based on the calculated pore-water concentration of each compound. The predicted pore-water concentrations for FLU were 38 and 21 μg/L for Lakes Erie and Huron sediments, respectively; and for TF, these concentrations were 30 μg/L in Lake Erie sediments and 17 μg/L in Lake Huron sediments calculated from the equations in Di Toro et al. [27] using the log K_{ow} values of 5.2 for FLU and 5.3 for TF [28]. These concentrations equate to dissolved (i.e., nonsorbed) percentages of <0.1% of the mass of FLU or TF spiked onto either sediment at 100 mg/kg.

Given the above assumption, a likely explanation for the observed lower desorption at lower treatment concentrations over the duration of the experiment (34 d) is related to the types of binding sites available for the contaminants in the sediment organic matrix. The triphasic kinetic model applied to the desorption data is not a mechanistic description of desorption. It conceptually describes binding sites from which contaminants desorb rapidly, slowly, or very slowly. The activation enthalpies required for desorption from these sites range from nearly zero (rapid) to high (60–100 kJ/mol; slow and very slow) [7,21]. In a recent review, Pignatello and Xing [6] reported that the slow fraction(s) of desorption depended on the inverse of the initial applied concentrations. More simply, this means that, as the concentration of contaminants in the sediments declines, the slow desorption of hydrophobic organic chemicals is dominant. This effect at low contaminant

Table 4. Times at which 99.9% ($t_{99.9}$) of the sediment-associated fluoranthene and trifluralin will be desorbed from the rapid, slow, and very slow desorption compartments[a]

Sediment	Compound	Desorption	Time[b]	Concentration (mg/kg) 10	40	100
Lake Erie, USA	Fluoranthene	Rapid	h	20.3	17.9	16.8
			d	0.844	0.744	0.700
			y	0.002	0.002	0.002
		Slow	h	276	270	251
			d	11.5	11.2	10.5
			y	0.032	0.031	0.029
		Very slow	h	31,399	36,357	46,052
			d	1,308	1,515	1,919
			y	3.58	4.15	5.26
	Trifluralin	Rapid	h	16.1	15.4	13.8
			d	0.670	0.641	0.576
			y	0.002	0.002	0.002
		Slow	h	270	265	270
			d	11.2	11.0	11.3
			y	0.031	0.030	0.031
		Very slow	h	24,671	23,820	27,631
			d	1,028	992	1,151
			y	2.82	2.72	3.15
Lake Huron, USA	Fluoranthene	Rapid	h	13.3	11.8	11.7
			d	0.553	0.491	0.487
			y	0.002	0.001	0.001
		Slow	h	221	202	219
			d	9.20	8.42	9.14
			y	0.025	0.023	0.025
		Very slow	h	25,584	30,034	36,357
			d	1,066	1,251	1,515
			y	2.92	3.43	4.15
	Trifluralin	Rapid	h	9.85	10.4	12.1
			d	0.411	0.435	0.504
			y	0.001	0.001	0.001
		Slow	h	217	227	258
			d	9.06	9.48	10.8
			y	0.025	0.026	0.029
		Very slow	h	16,447	19,736	20,317
			d	685	822	847
			y	1.88	2.25	2.32

[a] Calculated from the values of k_{rap}, k_{slow}, and k_{vs} using Equation 2.
[b] Time scales: h = hours; d = days; y = years.

concentrations is most likely because there are a limited number of high-affinity or high-energy-binding sites [29]. Higher sorption efficiencies are often observed at lower sorbate concentrations because of progressive saturation of the high-energy-binding sites as the concentration increases [30]. This, combined with kinetic hysteresis (i.e., slower rates of emptying than filling) following the binding of slowly desorbing sites, leads to slow desorption [6]. In the present study, F_{rap} tended to increase with increasing concentration from 10 to 100 mg/kg, which suggests that the more slowly desorbing, higher energy binding sites became limited with increasing contaminant concentration. Thus, the sorbed compounds at the lower concentrations proportionately occupied more of the slowly or very slowly desorbing compartments.

Differences between sediments

Desorption of FLU and TF from Lake Huron sediments (3.6% TOC) was faster than from the Lake Erie sediments (2.1% TOC) despite the higher organic carbon content of the former. We hypothesized that FLU and TF desorption rate constants would be inversely related to the amount of organic matter in the test sediments based on the findings of other investigations [1,31]. However, the opposite trend was observed.

With the failure of the organic carbon hypothesis, particle-size distribution of the contaminants was examined to explain the faster rates of FLU and TF desorption in Lake Huron sediments. Differential distribution of benzo[*a*]pyrene and hexachlorobiphenyl among sediment particles has been observed, with the largest fractions of the compounds being associated with relatively small particles, <63 μm [32]. Some investigators have demonstrated that desorption of contaminants increased inversely with particles size in physically manipulated (pulverized) sediments [33]. Others have shown no correlations between desorption kinetics and particle size, down to 1 μm in some cases, for polycyclic aromatic hydrocarbons, polychlorinated biphenyls, and pesticides in sediments and soils ([34] and references therein). In the present study, the percentage of small particles (<63 μm) was slightly higher in Lake Erie sediments (93.5%) than in sediments from Lake Huron (87.6%). A hypothesis that desorption rate constants of FLU and TF would be inversely related to particle size and thus would be higher for the Lake Erie sediments was not supported by the data.

Finally, the polarity of the organic matter in the sediments, as indicated by their C/N ratios, was evaluated to explain the higher desorption rate constants from the Lake Huron sediments. Many investigators have reported decreases in chemical

sorption and organic carbon sorption coefficients for hydrophobic organic chemicals with increasing polarity of the sediments [35–37]. In the present study, the C/N ratios were very similar between Lake Erie (5.87–6.31) and Lake Huron (5.67–6.61). Thus, the polarity of the sediment organic matter did not explain the observed difference in desorption rate constants between sediments.

Because a reason for the higher desorption rate constants observed for the Lake Huron sediments was not provided through other measurements taken during the study (e.g., TOC, particle-size distribution, C/N ratio), then some other characteristic of the sediments and/or sediment organic content was responsible for this difference. The samples of sediments used in the present study were from two different sources on the Great Lakes, and thus the differences in the type, age, and quality of the organic matter in these samples (as indicated by measures of the following characteristics: concentrations of pigments, total amino acids, lignin-derived phenols, and lipids; absorptivity at 270 nm [38]) may have been responsible for the observed differences in desorption rates. These differences may have been due to distributions or amounts of structurally distinct soft carbon, which is analogous to a more flexible or rubbery polymer, and hard carbon, which is more like a glassy polymer [39]. Differences such as these are thought to control the amounts of rapidly (soft carbon) and slowly (hard carbon) desorbing sites within the sediment organic matrix [5,19,40]. Research on these specific aspects of organic carbon and their roles in desorption is a continuing area of study.

Utility of desorption data

The present study provided estimates of the rate constants of desorption and fractional distributions of FLU and TF among the rapid, slow, and very slow compartments after nearly four months equilibration. Because these rate estimates were determined during constant mixing of spiked sediments at a stable temperature (22°C) in the presence of a strong sink (Tenax), they are considered to represent maximum rate constants of desorption. The method used here also assumes that the rates are constant for each compartment, whereas rates of desorption in the field can change with time [6]. These artifacts increase the uncertainty in our current ability to predict desorption and hence bioavailability and acceptable remediation levels in the field from laboratory data, especially because very little of the rapidly desorbing fractions often remain in aged and weathered contaminated field sediments [8]. However, the estimated values of the rapid, slow, and very slow desorption rate constants of FLU and TF were within the ranges reported for hydrophobic organic chemicals in the literature (i.e., k_{rap}, 10^{-1}/h; k_{slow}, $10^{-2\text{–}3}$/h; k_{vs}, 10^{-4}/h) from both laboratory- and field-contaminated sediments and soils [8,24,41]. Therefore, it is reasonable to assume that the $t_{99.9}$ values (Table 4) that were calculated for FLU and TF give a realistic indication of the persistence of these contaminants in field sediments both after an input event and after aging of the sediments as desorption of most of the fast fraction occurs within hours and can take years for the very slowly desorbing fraction [8].

The fraction of sediment-associated contaminants in the rapidly desorbing compartment is increasingly considered to be bioavailable for accumulation or biodegradation [9–11]. Recently, a proposed method for determining the bioavailable concentrations of hydrophobic organic chemicals was based on the rapidly desorbing fraction, whereby $F_{rap} \cdot C_{sediment}$ provides a better estimate than equilibrium partitioning equations [7,12]. Some authors suggest that there is little or no uptake in biota from the slowly and very slowly desorbing fractions [12]. This generalization should be viewed with caution, however, as pore water is assumed to be the dominant route of uptake and thus uptake by ingestion, which has been shown to be important to deposit-feeding benthic species [42], is ignored. Therefore, based on the values of F_{rap} for FLU and TF in the present study, for which the aging time was relatively short, the bioavailable concentration in the sediments would be roughly predicted to range from approximately 31 to 47% of the measured concentrations of FLU and from 40 to 55% of the bulk sediment levels of TF.

Conclusion

The triphasic model of desorption provided estimates of F_{rap}, k_{rap}, F_{slow}, k_{slow}, F_{vs}, and k_{vs} for FLU and TF that are similar to previously reported values of these parameters for hydrophobic organic chemicals. The rapidly desorbing fraction for FLU and TF in sediments that were aged for four months ranged from 31 to 55% of the initial concentrations and k_{rap}, k_{slow}, and k_{vs} values were on the order of 10^{-1}/h, 10^{-3}/h, and 10^{-4}/h, respectively. The total fraction of the initial contaminant amount that desorbed over the time course was directly related to concentration, even though the mass of organic carbon in the sediments far exceeded (by a factor of 50–90) the applied masses of the test chemicals. It was postulated that this trend was due to the combined effects of saturation of high-energy (slow and very slow) binding sites in the organic carbon matrix and hysteresis. Higher rate constants of desorption were observed for FLU and TF from the Lake Huron sediments and this was not apparently related to the TOC, particle-size distribution, or polarity (C/N ratio) of the sediments. A reasonable explanation for this difference between the sediment types would be that the relative amounts of soft and hard carbon were dissimilar for Lakes Erie and Huron sediments. Laboratory-to-field extrapolations are difficult, but overall, FLU and TF were predicted to persist for years due to the very slow desorption of an estimated 30.5 to 52.9% of the bulk sediment concentrations. Finally, based on the rapidly desorbing fractions, bioavailable amounts of the contaminants were predicted to be between 31 to 55% of sediment concentrations.

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REFERENCES

1. Karickhoff SW, Brown DS, Scott TA. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Res* 13:241–248.
2. Mihelcic JR, Lueking DR, Mitzell RJ, Stapleton JM. 1993. Bioavailability of sorbed- and separate-phase chemicals. *Biodegradation* 4:141–153.
3. Landrum PF, Eadie BJ, Faust WR. 1992. Variation in the bioavailability of polycyclic aromatic hydrocarbons to the amphipod *Diporeia* (spp.) with sediment aging. *Environ Toxicol Chem* 11: 1197–1208.
4. Alexander M. 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ Sci Technol* 34: 4259–4265.
5. Luthy RG, Aiken GR, Brusseau ML, Cunningham SD, Gschwend PM, Pignatello JJ, Reinhard M, Traina SJ, Weber WJ Jr, Westall

JC. 1997. Sequestration of hydrophobic organic contaminants by geosorbents. *Environ Sci Technol* 31:3341–3347.
6. Pignatello JJ, Xing B. 1996. Mechanisms of slow sorption of organic chemicals to natural particles. *Environ Sci Technol* 30: 1–11.
7. Cornelissen G. 1999. Mechanism and consequences of slow desorption of organic compounds from sediments. PhD thesis. University of Amsterdam, Amsterdam, The Netherlands.
8. ten Hulscher TEM, Vrind BA, Van den Heuvel H, Van der Velde LE, Van Noort PCM, Beurskens JEM, Govers HAJ. 1999. Triphasic desorption of highly resistant chlorobenzenes, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons in field contaminated sediment. *Environ Sci Technol* 33:126–132.
9. Kraaij RH, Ciarelli S, Tolls J, Kater BJ, Belfroid A. 2001. Bioavailability of lab-contaminated and native polycyclic aromatic hydrocarbons to the amphipod *Corophium volutator* relates to chemical desorption. *Environ Toxicol Chem* 20:1716–1724.
10. Kraaij RH, Tolls J, Sijm D, Cornelissen G, Heikens A, Belfroid A. 2002. Effects of contact time on the sequestration and bioavailability of different classes of hydrophobic organic chemicals to benthic oligochaetes (Tubificidae). *Environ Toxicol Chem* 21: 752–759.
11. Lamoureux EM, Brownawell BJ. 1999. Chemical and biological availability of sediment-sorbed hydrophobic organic contaminants. *Environ Toxicol Chem* 18:1733–1741.
12. van Noort PCM, Cornelissen G, ten Hulscher D. 1999. Sediment quality criteria, bioavailability, and sorptive attenuation of organic compounds. *SETAC—Europe News* 10:16–17.
13. Cornelissen G, van Noort PCM, Govers HAJ. 1997. Desorption kinetics of chlorobenzenes, polycyclic aromatic hydrocarbons, and polychlorinated biphenyls: Sediment extraction with Tenax® and effects of contact time and solute hydrophobicity. *Environ Toxicol Chem* 16:1351–1357.
14. Ditsworth GR, Schults DW, Jones JKP. 1990. Preparation of benthic substrates for sediment toxicity testing. *Environ Toxicol Chem* 9:1523–1529.
15. Northcott GL, Jones KC. 2000. Spiking hydrophobic organic compounds into soil and sediment: A review and critique of adopted procedures. *Environ Toxicol Chem* 19:2418–2430.
16. Greenberg MS. 2002. Defining benthic organism exposure: Bioavailability and effects of non-polar organics. PhD thesis. Wright State University, Dayton, OH, USA.
17. Walker WW, Cripe CR, Pritchard PR, Bourquin AW. 1988. Biological and abiotic degradation of xenobiotic compounds in in vitro estuarine water and sediment/water systems. *Chemosphere* 17:2255–2270.
18. Pignatello JJ. 1990. Slowly reversible sorption of aliphatic halocarbons in soils, I: Formation of residual fractions. *Environ Toxicol Chem* 9:1107–1115.
19. Cornelissen G, Rigterink H, van Noort PCM, Govers HAJ. 2000. Slowly and very slowly desorbing organic compounds in sediments exhibit Langmuir-type sorption. *Environ Toxicol Chem* 19: 1532–1539.
20. L'Annunziata MF, Kessler MJ. 1998. Radiotracer liquid scintillation analysis. In L'Annunziata MF, ed, *Handbook of Radioactivity Analysis.* Academic, San Diego, CA, USA, pp 209–329.
21. Cornelissen G, van Noort PCM, Parsons JR, Govers HAJ. 1997. Temperature dependence of slow adsorption and desorption kinetics of organic compounds in sediments. *Environ Sci Technol* 31:454–460.
22. Ratkowsky DA. 1983. *Nonlinear Regression Modeling: A Unified Practical Approach.* Marcel Dekker, New York, NY, USA.
23. Opdyke DR, Loehr RC. 1999. Determination of chemical release rates from soils: Experimental design. *Environ Sci Technol* 33: 1193–1199.
24. Cornelissen G, Rigterink H, ten Hulscher DEM, Vrind BA, van Noort PCM. 2001. A simple Tenax® extraction method to determine the availability of sediment-sorbed organic compounds. *Environ Toxicol Chem* 20:706–711.
25. Golab T, Occolowitz JL. 1979. Soil degradation of trifluralin: Mass spectrometry of products and potential products. *Biomed Mass Spectrom* 6:1–9.
26. Smith AE, Aubin AJ, Derksen DA. 1988. Loss of trifluralin from clay and loam soils containing aged and freshly applied residues. *Bull Environ Contam Toxicol* 41:569–573.
27. Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ Toxicol Chem* 10:1541–1583.
28. Mackay D, Shiu W-Y, Ma K-C. 1997. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals,* Vol V, *Pesticide Chemicals.* Lewis, Boca Raton, FL, USA.
29. Schlebaum W, Schraa G, Van Riemsdijk WH. 1999. Influence of nonlinear sorption kinetics on the slow-desorbing organic contaminant fraction in soil. *Environ Sci Technol* 33:1413–1417.
30. Weber JB, Miller CT. 1989. Organic chemical movement over and through soil. In Sawhney BL, Brown K, eds, *Reactions and Movement of Organic Chemicals in Soils.* Special Publication 22. Soil Science Society of America, Madison, WI, pp 305–334.
31. Kan AT, Fu G, Hunter M, Chen W, Ward CH, Tomson MB. 1998. Irreversible sorption of neutral hydrocarbons to sediments: Experimental observations and model predictions. *Environ Sci Technol* 32:892–902.
32. Kukkonen J, Landrum PF. 1996. Distribution of organic carbon and organic xenobiotics among different particle-size fractions in sediments. *Chemosphere* 32:1063–1076.
33. Ball WP, Roberts PV. 1991. Long-term sorption of halogenated organic chemicals by aquifer material. 2. Intraparticle diffusion. *Environ Sci Technol* 25:1237–1249.
34. Cornelissen G, van Zuilen H, van Noort PCM. 1999a. Particle size dependence of slow desorption of in situ PAHs from sediments. *Chemosphere* 38:2369–2380.
35. Grathwohl P. 1990. Influence of organic matter from soils and sediments from various origin on the sorption of some chlorinated aliphatic hydrocarbons: Implications on K_{oc} correlations. *Environ Sci Technol* 24:1687–1693.
36. Xing B, McGill WB, Dudas MJ. 1994. Cross-correlation of polarity curves to predict partition coefficients of nonionic organic contaminants. *Environ Sci Technol* 28:1929–1933.
37. Landrum PF, Gossiaux DC, Kukkonen J. 1997. Sediment characteristics influencing the bioavailability of nonpolar organic contaminants to *Diporeia* spp. *Chem Speciat Bioavailab* 9:43–55.
38. Kukkonen JVK, Landrum PF, Mitra S, Gossiaux DC, Gunnarsson J, Weston D. 2003. Sediment characteristics affecting desorption kinetics of select PAH and PCB congeners for seven laboratory spiked sediments. *Environ Sci Technol* 37:4656–4663.
39. Huang WL, Young TM, Schlautman MA, Yu H, Weber WJ. 1997. A distributed reactivity model for sorption by soils and sediments. 9. General isotherm nonlinearity and applicability of the dual reactive domain model. *Environ Sci Technol* 31:1703–1710.
40. LeBoeuf EJ, Weber WJ. 1999. Reevaluation of general partitioning model for sorption of hydrophobic organic contaminants by soil and sediment organic matter. *Environ Toxicol Chem* 18:1617–1626.
41. McCall PJ, Agin GL. 1985. Desorption kinetics of picloram as affected by residence time in the soil. *Environ Toxicol Chem* 4: 37–44.
42. Leppänen MT, Kukkonen JVK. 1998b. Relative importance of ingested sediment and pore water as bioaccumulation routes for pyrene to oligochaete (*Lumbriculus variegatus*, Muller). *Environ Sci Technol* 32:1503–1508.